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Magneto- to electro-active transmutation of spin waves in ErMnO_3

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The low energy dynamical properties of the multiferroic hexagonal perovskite ErMnO_3 have been studied by inelastic neutron scattering as well as terahertz and far infrared spectroscopies on synchrotron source. From these complementary techniques, we have determined the magnon and crystal field spectra and identified a zone center magnon only excitable by the electric field of an electromagnetic wave. Using comparison with the isostructural YMnO_3 compound and crystal field calculations, we propose that this dynamical magnetoelectric process is due to the hybridization of a magnon with an electro-active crystal field transition.

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The term magnetoelectric (ME) makes reference to a variety of phenomena in which electric dipoles and magnetic moments are mutually linked [1]. ME processes attract a considerable research interest, largely driven by their potential use in future information technologies [1, 2] and, more recently, by their interpretation in terms of exotic magnetic and ME monopoles [3]. A ME process that is particularly striking is the electric-charge dressing of spin-waves that gives rise to electrically active magnons (or electromagnons) [4]. This dynamical ME effect has been most clearly demonstrated in multiferroic materials such as RMnO_3 [5], RMn_2O_5 [6], CuFeO_2 [7], and BiFeO_3 [8]. The ME dual of electromagnons, that is magneto-active excitations of the lattice, have also been recently reported [9]. This type of hybrid excitations enable additional optical functionalities such as directional light switching and quadrochromism [10] that open new perspectives in photonics and magnonics [11].

Several microscopic mechanisms have been identified behind the ME character of these hybrid excitations. In essence, they all trace back to the specific couplings between spins and the deformable lattice that can produce ferroelectricity. In orthorhombic RMnO_3 , for example, both the so-called inverse Dzyaloshinskii-Moriya and Heisenberg exchange mechanisms contribute to the static polarization [12] and also generate different electromagnons [5]. In hexagonal YMnO_3 , a phonon-magnon anticrossing has been observed revealing that lattice and spins are dynamically coupled in this system too [13, 14]. However, the ME nature of this feature was not been proven and, to the best of our knowledge, no electromagnon has been reported so far in the other members of this family of prominent multiferroics [15–17]. In this

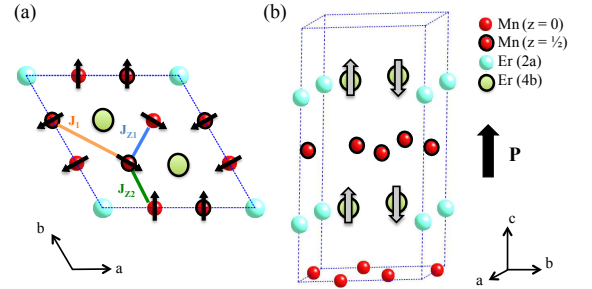


FIG. 1: Schematic illustration of ErMnO_3 crystallographic and magnetic structure in the temperature range $T'_N < T < T_N$ where Mn magnetic moments are ordered at 120° (a) and Er moments on the 4b site only are polarized in an antiferromagnetic arrangement (b). This multiferroic phase presents an electric polarisation \mathbf{P} along the \mathbf{c} -axis. The exchange interactions involved in the Mn magnetic order are also shown.

Letter, we report on the presence of a new type of ME excitation in the hexagonal ErMnO_3 multiferroic compound. By means of complementary spectroscopic tools and the comparison with hexagonal YMnO_3 , we show evidence of the transmutation of a regular magnon to an electro-active excitation in ErMnO_3 . We ascribe this effect to a distinct hybridization mechanism between Mn^{3+} spin-waves and crystal field (CF) excitations of the Er^{3+} rare earth.

In ErMnO_3 , the ferroelectric state occurs below $T_c = 833$ K with a spontaneous polarization along the \mathbf{c} -axis (polar space group $P6_3cm$). Mn^{3+} ions, located on the 6c Wyckoff sites, form a triangular lattice in the (a, b) planes. A complex magnetic order with a 120° arrange-

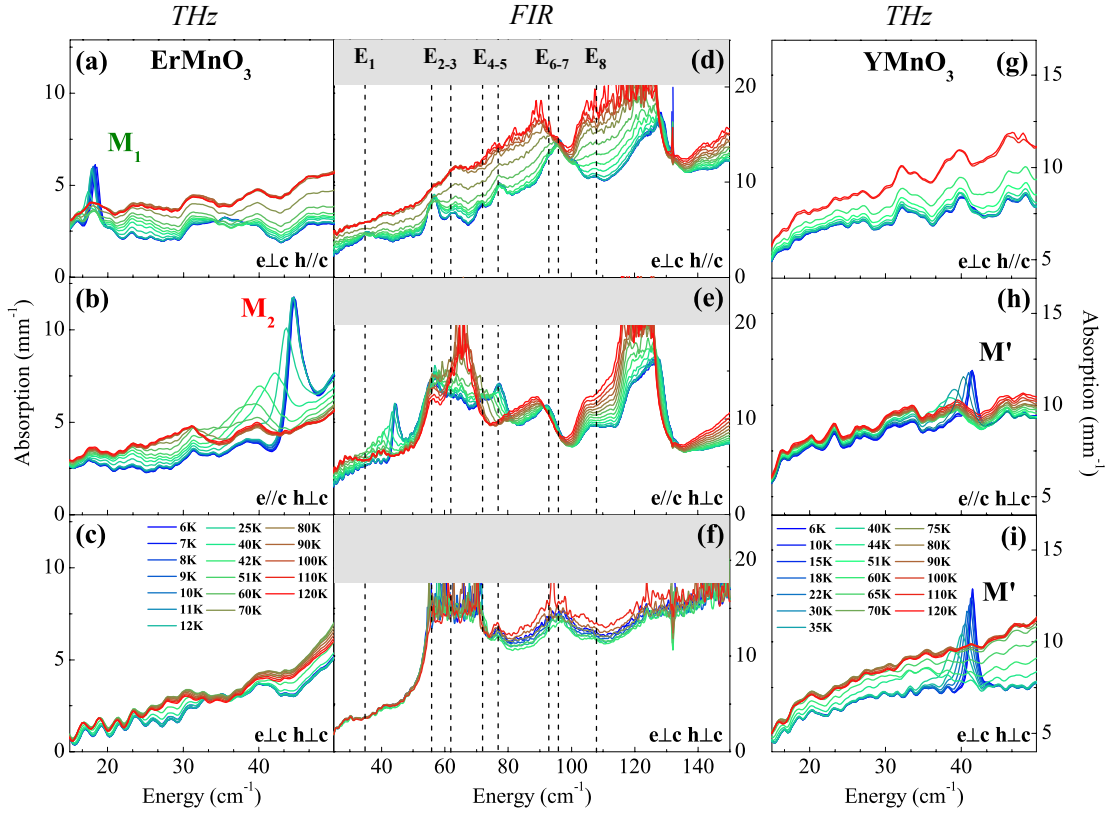


FIG. 2: THz (a,b,c) and FIR (d,e,f) absorption spectra of ErMnO_3 for the 3 different orientations of the electromagnetic wave \mathbf{e} , \mathbf{h} fields with respect to the crystal \mathbf{c} -axis, in the temperatures range 6 K - 120 K. The grey areas indicate regions where the absorption saturates. The various excitation modes discussed in the text are pointed out. THz (g,h,i) absorption spectra of YMnO_3 measured in the same conditions as ErMnO_3 .

ment in the (a, b) plane ($\mathbf{k} = \mathbf{0}$ propagation vector) takes place at $T_N = 79$ K, primarily produced by the Mn^{3+} magnetic moments (Γ_4 irreducible representation [18, 19]). On the other hand, the Er^{3+} ions occupy two distinct Wyckoff sites, $4b$ and $2a$ [20]. Below T_N , the $4b$ magnetic moments are orientated antiferromagnetically along the \mathbf{c} -axis, polarized in the molecular field of the Mn magnetic moments [21] (See Fig.1). Below $T'_N \approx 10$ K, the $2a$ magnetic moments order ferromagnetically along the \mathbf{c} -axis and produce a spin reorientation at the $4b$ rare-earth and Mn sites around 5 and 2 K respectively (Γ_2 irreducible representation [18, 19]). Besides its multiferroic properties, ErMnO_3 is particularly interesting because of the strong interplay between the Mn^{3+} ($3d^4$) magnetism and the Er^{3+} ($4f^{11}$) spins [18, 19].

We probed the dynamical properties of ErMnO_3 by inelastic neutron scattering and THz/FIR spectroscopies. Additionally, in order to confirm the strong influence of the Er magnetism on the dynamical properties of ErMnO_3 , we also measured the THz response of YMnO_3 where Er is replaced by non-magnetic Y. THz/FIR measurements were performed on the AILES beamline at SOLEIL Synchrotron using a Bruker IFS125 interferometer [22]. This technique allows to probe magnetic and

electric excitations, their characteristic energies as well as their selection rules as regards the electric (\mathbf{e}) and magnetic (\mathbf{h}) components of the polarized electromagnetic wave. For this purpose, two disks (thickness $\approx 500\mu\text{m}$, surface $\approx 12\text{ mm}^2$) were cut in the same single crystal grown by floating zone method in an image furnace, with the \mathbf{c} -axis in the plane and out of the plane perpendicular to the THz/FIR propagation vector. Using the same procedure as in [9], absorption spectra were obtained in the temperature 6 - 120 K with three different geometries: i) $\mathbf{e} \perp \mathbf{c}$ $\mathbf{h} \parallel \mathbf{c}$, ii) $\mathbf{e} \parallel \mathbf{c}$ $\mathbf{h} \perp \mathbf{c}$ and iii) $\mathbf{e} \perp \mathbf{c}$ $\mathbf{h} \perp \mathbf{c}$. The THz (10 - 50 cm^{-1}) and FIR (20 - 200 cm^{-1}) range were explored at a resolution of 0.5 cm^{-1} using the same 6 μm thick silicon-mylar beam splitter and two different bolometers.

Whereas these experiments mainly probe the Brillouin zone center, inelastic neutron scattering is sensitive to a large volume of the reciprocal space. A first experiment using unpolarized neutrons was performed at the Institut Laue-Langevin (ILL) high-flux reactor in Grenoble on the time-of-flight spectrometer IN5 with an incident wavelength of 2 Å for an energy resolution of 0.8 meV (7 cm^{-1}). To discriminate between the magnetic and nuclear contributions, we also used polarized neutrons and longitudinal polarization analysis on the CRG-CEA

triple-axis spectrometer IN22 installed at the ILL [19]. The final energy was kept fixed at 14.7 meV yielding an energy resolution of 1 meV (8 cm^{-1}). In both experiments, performed at 1.5 K and 20 K respectively, the ErMnO_3 single-crystal was oriented with the \mathbf{a} -axis vertical in order to survey the $(\mathbf{b}^*, \mathbf{c}^*)$ scattering plane.

Fig.2 gives an overview of the absorption spectra of ErMnO_3 (THz and FIR) and YMnO_3 (THz) and of their temperature dependence. In ErMnO_3 , two excitations \mathbf{M}_1 and \mathbf{M}_2 are clearly seen at low temperatures in the THz range (centered at 18.5 cm^{-1} and 44.6 cm^{-1} respectively at 6 K). The magnetic origin of these excitations is suggested by their softening and eventually disappearance at T_N . The first mode \mathbf{M}_1 is excited by the magnetic field $\mathbf{h} \parallel \mathbf{c}$, as expected for a magnon. The second excitation \mathbf{M}_2 , in contrast, disappears when the electric field changes from $\mathbf{e} \parallel \mathbf{c}$ to $\mathbf{e} \perp \mathbf{c}$, even if the magnetic field is kept $\mathbf{h} \perp \mathbf{c}$. This implies that, unexpectedly, \mathbf{M}_2 is excited by the electric field of the THz wave. In YMnO_3 a similar excitation \mathbf{M}' is also seen at approximately the same energy (41.5 cm^{-1} at 6 K). \mathbf{M}' , however, remains visible for $\mathbf{h} \perp \mathbf{c}$ irrespective of the orientation ($\mathbf{e} \perp \mathbf{c}$ or $\mathbf{e} \parallel \mathbf{c}$) of the electric field as already reported [23]. In fact, the comparison with the magnon dispersion curves analysed in [13, 17] confirms that \mathbf{M}' is a magnon involving spin components perpendicular to the \mathbf{c} -axis in agreement with its $\mathbf{h} \perp \mathbf{c}$ excitation rule. This highlights the peculiarity of the ErMnO_3 \mathbf{M}_2 excitation which is only excited by the electric field of the THz wave.

In addition to these modes, FIR ErMnO_3 spectra [24] reveal additional low-energy excitations persisting above T_N . Their number and intensity depend on the temperature and on the orientation of the electric/magnetic fields (see Fig.2). At low temperature, there is a first weak excitation at 35 cm^{-1} (\mathbf{E}_1). Then, there is a set of 4 excitations at $56, 62, 72$ and 77 cm^{-1} ($\mathbf{E}_2, \mathbf{E}_3, \mathbf{E}_4$ and \mathbf{E}_5) that merge into three excitations above T_N . Note that these signals are enhanced for $\mathbf{e} \parallel \mathbf{c}$ $\mathbf{h} \perp \mathbf{c}$ in the sample with in plane \mathbf{c} -axis. Next, the two close excitations at 93 and 96 cm^{-1} (\mathbf{E}_6 and \mathbf{E}_7) also merge into a single one above T_N . Another excitation is visible around 108 cm^{-1} (\mathbf{E}_8). We note that this identification is consistent with the modes reported in reference 16 from FIR spectroscopy, except for the weaker modes \mathbf{E}_1 and \mathbf{E}_8 [25]. Finally, around 125 cm^{-1} a larger phononic band is observed in agreement with Ab initio calculation [26] and Raman spectroscopy [27].

The observed ErMnO_3 excitations can be either of magnonic origin, either due to transitions between CF levels of the two Er ion types, or from phonons. Inelastic neutron scattering allows to further identify their origin. Fig.3a presents IN5 measurements at 1.5 K along the $(0 k 0)$ direction. A dispersive signal emerges from the two $(0 1 0)$ and $(0 2 0)$ zone centers and corresponds to spin-waves associated to the Mn^{3+} magnetic order. This signal was well characterized combining IN5 and

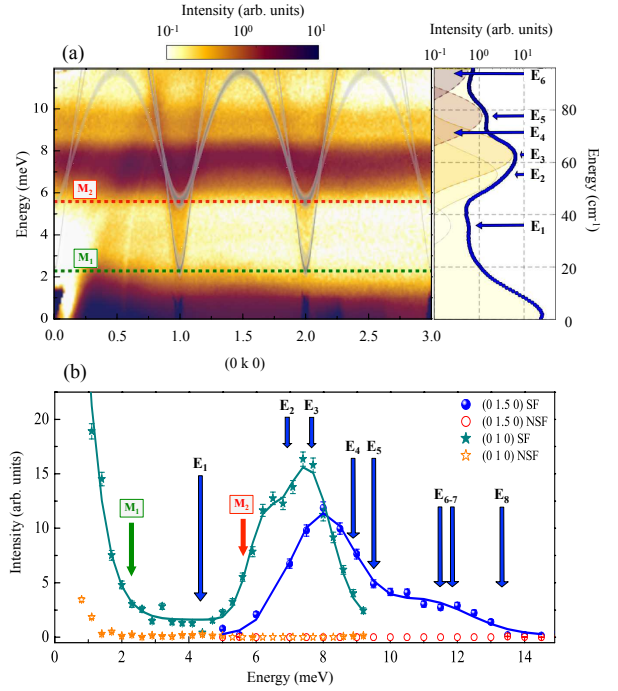


FIG. 3: (a)Left: IN5 inelastic neutron signal spectrum recorded at 1.5 K along $(0 k 0)$, the data were cut and integrated in a reciprocal space part, from $\ell = -2$ to $+2$ along the \mathbf{c}^* direction. The calculated Mn spin-waves dispersion (identical for Γ_2 or Γ_4) are reported (continuous lines). The corresponding Hamiltonian involves three exchange interactions, one in-plane first neighbor $J_1 = 2.65 \text{ meV}$, and two out-of-plane interactions J_{z1} and J_{z2} with $J_{z1} - J_{z2} = -0.007 \text{ meV}$ (see Fig.1), as well as two anisotropy terms at $D = 0.39 \text{ meV}$ and $h = 0.055 \text{ meV}$ producing the energy gaps for the spin components in and perpendicular to the (\mathbf{a}, \mathbf{b}) plane respectively. Right: corresponding energy map obtained by powder-average of all single crystal spectra; all scattering angles were grouped assuming nearly non dispersive CF excitations (b) IN22 spin flip and non spin flip neutron scattering signals recorded at 20 K at the $(0 1 0)$ zone center and $(0 1.5 0)$ zone boundary. The magnon modes \mathbf{M}_i and CF transitions \mathbf{E}_i observed in THz and FIR spectroscopy are also shown.

IN22 measurements and can be reproduced by spin-wave calculations in the linear approximation of the Holstein-Primakoff formalism [28], using the same Hamiltonian as in reference 21 (see the continuous lines in Fig.3a and reference 19). The neutron signal is broadened by convolution to the limited experimental resolution in these instrumental configurations.

In the $(0 k 0)$ zone centers, the spin wave of the lowest branch at 18 cm^{-1} is gapped due to the coupling between the Mn and the anisotropic Er ions and correlates spin components along the \mathbf{c} -axis at the $(0 0 0)$ zone center. It thus agrees with the \mathbf{M}_1 THz mode excited by $\mathbf{h} \parallel \mathbf{c}$. Note that this gap is reduced in YMnO_3 where the lowest branch lies out of the range of the THz measurements. In ErMnO_3 , the higher energy branch is calculated at 45

cm^{-1} , which corresponds well to the \mathbf{M}_2 excitation and is similar to the one observed in YMnO_3 at 41.5 cm^{-1} . The calculations show that it involves spin components perpendicular to the \mathbf{c} -axis and should therefore be observed for $\mathbf{h} \perp \mathbf{c}$, as it is the case in YMnO_3 . However it is not observed experimentally in the configuration $\mathbf{e} \perp \mathbf{c}$ $\mathbf{h} \perp \mathbf{c}$ in ErMnO_3 . The \mathbf{M}_2 excitation is therefore sensitive to the electric component of the incident wave, although it has a magnetic origin since it coincides with the energy of a magnon and disappears above T_N .

The Mn spin-waves dispersive signal goes through flatter broad excitations. A closer look using the integrated intensity in the $(0 \text{ k } 0)$ direction (left panel in Fig.3a) allows to distinguish 5 excitation modes corresponding to those observed in THz and FIR spectroscopy. Moreover, as shown from measurements with polarized neutron at 20 K (Fig.3b), these modes have essentially a s spin-flip character i.e. associated with magnetic scattering, and are thus attributed to CF level transitions. They correspond to \mathbf{E}_1 (35 cm^{-1}), to \mathbf{E}_2 and \mathbf{E}_3 (60 cm^{-1}), to \mathbf{E}_4 and \mathbf{E}_5 (75 cm^{-1}), to \mathbf{E}_6 and \mathbf{E}_7 (97 cm^{-1}) and to \mathbf{E}_8 , all observed with a better energy resolution in FIR measurements. Last, the neutron scattering experiments also reveal the strong coupling between the Mn^{3+} and Er^{3+} $4b$ magnetism at the dynamical level with, in particular, a noticeable modulation of the 60 cm^{-1} broad band at the crossing points with the Mn^{3+} spin-waves. Another indication of this coupling is the Zeeman splitting of CF levels seen in FIR spectroscopy below T_N , and also reported in reference 16, produced by the molecular field arising from the Mn magnetic order: the four \mathbf{E}_2 to \mathbf{E}_5 excitations and the levels around 98 cm^{-1} (\mathbf{E}_6 and \mathbf{E}_7) probably results from three excitations and from a single one respectively through cooling below T_N .

From the above experimental determination of magnons and CF transitions scheme in ErMnO_3 , we can now discuss the nature of the remarkable electro-active excitation \mathbf{M}_2 . The equivalent excitation behaves as a standard magneto-active magnon in YMnO_3 . This difference suggests that the electrical activity of the \mathbf{M}_2 excitation in ErMnO_3 is associated to the magnetic coupling between the magnetic rare earth and the Mn ions. It is known that a transition between CF levels of a rare-earth ion with a non-centrosymmetric point group can be either electro-active, or magneto-active, or both [29]. Then, by hybridization, a magnetoelectric CF excitation can transfer its electro-activity to a magnon. This mechanism was already proposed in HoMn_2O_5 and $\text{Tb}_3\text{Fe}_5\text{O}_{12}$ from FIR measurements [30, 31]. In order to test the validity of this scenario in ErMnO_3 , the Er^{3+} ($J=15/2$) CF levels were calculated using a point charge model [32, 33], taking into account the 7 O^{2-} closer neighbors of the two Er sites, with screening factors [34], fitted to recover the experimentally identified CF levels. The influence of a magnetic field was also computed to account for the splitting of the CF levels due to the coupling of the Er $4b$

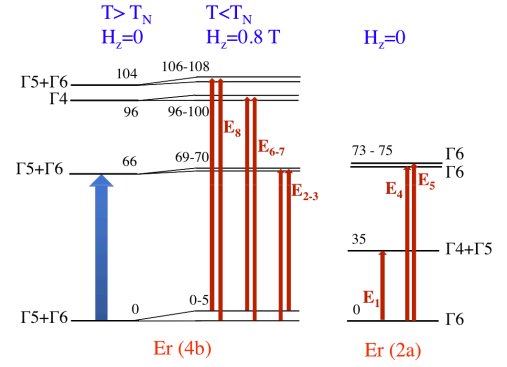


FIG. 4: Crystal field calculation from a point charge model for the two $4b$ and $2a$ Er^{3+} sites. The CF levels are labelled according to the irreducible representations of the double point groups associated with each Er sites. The splitting produced by a magnetic field of 0.8 T mimics the effect of the Mn molecular field on $\text{Er}(4b)$ CF levels, which occurs below T_N . The CF levels scheme consists in 9 doublets for each sites. The modes above 200 cm^{-1} are not shown. Note that the energy of the levels is very sensitive to the O^{2-} coordinates, which were obtained from single-crystal neutron diffraction at 10 K [19]. The observed THz and FIR transitions \mathbf{E}_i are shown (red arrows) as well as the possible excitation involved in the hybridization with a Mn magnon (blue arrow).

with the Mn. The results are reported in Fig.4 and show that, within this simple model, a qualitative agreement is obtained with the experiment as regards the position and number of modes. Moreover, a symmetry analysis reveals that the two Er^{3+} sites can have CF level transitions that are both electro- and magneto-active. Specifically, transitions between levels belonging to the same (different) irreducible representation of the point group symmetry can be activated by $\mathbf{e} \parallel \mathbf{c}$ and $\mathbf{h} \parallel \mathbf{c}$ ($\mathbf{e} \perp \mathbf{c}$ and $\mathbf{h} \perp \mathbf{c}$). In view of this, the absence of the \mathbf{M}_2 excitation in the THz $\mathbf{e} \perp \mathbf{c}$ and $\mathbf{h} \perp \mathbf{c}$ configuration suggests that the hybridization occurs between the magnetically coupled Mn and Er $4b$ through a CF transition allowed for $\mathbf{e} \parallel \mathbf{c}$. A possible transition is the one between the ground state level and the first excited level of $\text{Er}(4b)$, which is split below T_N [35].

In conclusion, we have observed the complete loss of the magnetic character of a magnon in ErMnO_3 transmuted to an electro-active excitation. We attribute this ME dynamical process to the hybridization between a CF level transition of the Er magnetic rare earth and a Mn magnon. This mechanism may be very general to other rare-earth based multiferroics. This exemplifies the richness of the emerging field of ME excitations and suggests new possibilities to manipulate these excitations, as for instance through the action of magnetic/electric static fields, that may dehybridized the CF transition and the magnon.

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in the $\mathbf{h} // \mathbf{c}$ channel may be due to the different strength of the electroactive versus magnetoactive processes.